

## Method for producing titanium dioxide

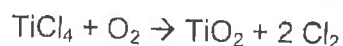
### 5 Field of the invention

The invention relates to the manufacture of titanium dioxide by oxidation of titanium tetrachloride, where liquid titanium tetrachloride is used.

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### Technological background of the invention

In one of the commercially used methods for manufacturing titanium dioxide pigment particles, known as the chloride process, titanium tetrachloride ( $\text{TiCl}_4$ ) is reacted with an oxidising gas, such as oxygen, air, etc., and with certain additives in a plug flow reactor to form titanium dioxide and chlorine gas:



The  $\text{TiO}_2$  particles are subsequently separated from the chlorine gas. Known additives are  $\text{AlCl}_3$  as a rutilising agent and steam or alkali salts as a nucleating agent.

20 Owing to the high activation energy of  $\text{TiCl}_4$  oxidation, the educts must be heated to such a degree that an adiabatic mixed temperature of the educts of approx. 800 °C is reached before the onset of the reaction so that the reaction takes place completely. The oxidation reaction is highly exothermal, meaning that, following complete, adiabatic conversion, the temperature of the product stream is roughly 900 °C higher than that of the educts. Before 5 the  $\text{TiO}_2$  particles are separated from the gaseous reaction products with the help of a filter, this mixture has to be substantially cooled in a cooling section in order to avoid damage to the filter.

According to US 3,615,202, oxygen and  $\text{TiCl}_4$  are preheated and subsequently caused to 30 react in a plug flow reactor. Since the full quantities of the educts are in each case added at one point of the plug flow reactor, this can be referred to as a single-stage method. Similarly, EP 0 427 878 B1 discloses a single-stage method in which oxygen is heated to roughly 1,500 °C to 1,650 °C and mixed with  $\text{TiCl}_4/\text{AlCl}_3$  vapour having a temperature of roughly 450 °C. The process is energetically unsatisfactory in both cases because, referred to the 100% 35 energy input for heating the educts, roughly 160 % thermal reaction energy is subsequently released. Roughly 210 % thermal energy then has to be dissipated from the hot product

stream in the cooling section. The substantial reaction enthalpy is thus not used for activating the reaction, but transferred to the cooling-water system.

In the single-stage method according to GB 969,618  $\text{TiCl}_4$  is introduced co-axially and the hot oxygen containing gas is introduced tangentially into the reactor. The  $\text{TiCl}_4$  is introduced in gaseous or liquid form.

For the purpose of energetic optimisation, EP 0 583 063 B1 describes two-stage introduction of  $\text{TiCl}_4$  into the reactor.  $\text{TiCl}_4$  with a temperature of at least  $450^\circ\text{C}$  and mixed with  $\text{AlCl}_3$  is fed into the hot oxygen stream at a first inlet point, and  $\text{TiCl}_4$  with a temperature of  $350^\circ\text{C}$  to  $400^\circ\text{C}$  and without  $\text{AlCl}_3$  at a further inlet point.

The method according to EP 0 852 568 B1 provides for not only the  $\text{TiCl}_4$  to be added in two stages, but also the oxygen. However, the object of this method is effective control of the mean  $\text{TiO}_2$  particle size, and thus of the tone of the  $\text{TiO}_2$  pigment base material. In this case,  $\text{TiCl}_4$  vapour having a temperature of roughly  $400^\circ\text{C}$  is first fed into an oxygen stream with a temperature of roughly  $950^\circ\text{C}$ . The  $\text{TiO}_2$  particles are formed, and particle growth takes place, in the downstream reaction zone.  $\text{TiCl}_4$  vapour heated to a lesser extent (approx.  $180^\circ\text{C}$ ) is added at a second inlet point. Oxygen having a temperature between  $25^\circ\text{C}$  and  $1,040^\circ\text{C}$  is introduced at the second inlet point, the temperature of the mixture being sufficient to initiate the reaction.

The multi-stage method according to US 6,387,347 is additionally said to reduce agglomeration. To this end, the previously heated  $\text{TiCl}_4$  stream is split into two part streams before addition to the reactor. One part stream is oxidised in the first stage of the reactor. The second part stream is cooled by injection of liquid  $\text{TiCl}_4$  (de-superheating) and then added to the reactor. De-superheating takes place outside the reactor, the temperature not falling below the condensation temperature of the overall stream.

US 2007/0172414 A1 discloses a multi-stage method for the reaction of  $\text{TiCl}_4$  and  $\text{O}_2$  in which gaseous  $\text{TiCl}_4$  is fed into the reactor in the first stage, and liquid  $\text{TiCl}_4$  in the second stage. This method permits energy savings and improvement of the particle size range.

Object and summary of the invention

The object of the present invention is to create a method for manufacturing titanium dioxide by oxidation of titanium tetrachloride that permits further energy savings compared to the methods known from the prior art.

5 The object is solved by a method for manufacturing titanium dioxide particles by reacting titanium tetrachloride with an oxygen-containing gas in a plug flow reactor, wherein the titanium tetrachloride is introduced into the reactor in at least two stages and is used exclusively in liquid form, as well as by the titanium dioxide particles manufactured according to this method.

10 Further advantageous embodiments of the invention are described in the sub-claims.

#### Brief description of the drawings

The following figures serve for a better understanding and for advantageous embodiments of the invention:

Figure 1 : diagrammatic illustration of a plug flow reactor having a single fluid nozzle, aligned parallel to a plane lying perpendicular to the center line of the reactor.

Figure 2 : side view of the reactor shown in Figure 1.

Figure 3 : diagrammatic illustration of a plug flow reactor having a hollow-core cluster head nozzle.

Figure 4: enlarged view of the nozzle shown in Figure 3.

Figure 5: diagrammatic illustrative of a plug flow reactor having three single fluid nozzles, aligned radially to the circumference of the reactor and parallel to a plane lying perpendicular to the center line of the reactor.

15 Figure 6: diagrammatic illustrative of a plug flow reactor having three single fluid nozzles, aligned tangentially to the circumference of the reactor and parallel to a plane lying perpendicular to the center line of the reactor.

#### Description of the invention

20 The method according to the invention differs from the aforementioned single-stage or multi-stage chloride processes for manufacturing titanium dioxide from the prior art in that the  $\text{TiCl}_4$  is introduced into the oxidation reactor in at least two stages and exclusively in liquid form.

In this context, the total quantity of liquid  $\text{TiCl}_4$  used is split up in several stages in that way, that only a small quantity is added in the first stage in order to start combustion despite using the liquid phase. In the first phase, the activation energy required is provided solely via the preheated oxygen. In all other stages, the activation energy is provided by the preheated oxygen and the reaction enthalpy of  $\text{TiCl}_4$  oxidation released in the upstream stages.

When developing the method, it is of central importance that the reaction not be extinguished as a result of injecting an excessive quantity of liquid  $\text{TiCl}_4$  into one of the stages. An effective indication of whether the reaction will run spontaneously or die out is provided by the calculated adiabatic mixed temperature of all educts in the respective stage before the start of the reaction. Experience shows that the reaction takes place completely upwards of an adiabatic mixed temperature of approx.  $740^\circ\text{C}$ . On this basis, the person skilled in the art can easily define the number of stages required and the distribution of the  $\text{TiCl}_4$  among these stages.

Surprisingly, the chloride process according to the invention, with addition of  $\text{TiCl}_4$  purely in liquid form, can be performed not only when using oxygen preheated to roughly  $1,600^\circ\text{C}$ , but also when using preheated oxygen having a temperature in the range from roughly  $740^\circ\text{C}$  to  $1,000^\circ\text{C}$ . In the latter case, there is no need for additional oxygen heating with an auxiliary flame, e.g. with toluene. A further advantage of the second version is lower chlorine consumption, which otherwise occurs due to formation of  $\text{HCl}$  during toluene combustion.

The method according to the invention can be performed under the conditions indicated in Examples 1 and 2, below, although this list is in no way intended to restrict the invention. The Reference Example is based on one-stage addition of gaseous  $\text{TiCl}_4$  in accordance with the prior art (EP 0 427 878 B1):

|                                                                         | Example 1 | Example 2 | Reference |
|-------------------------------------------------------------------------|-----------|-----------|-----------|
| No. of stages                                                           | 2         | 5         | 1         |
| $\text{O}_2$ temperature upstream of reaction zone ( $^\circ\text{C}$ ) | 1,650     | 920       | 1,650     |
| Toluene demand (kg/h)                                                   | 110       | 0         | 110       |
| Cl consumption due to $\text{HCl}$ formation (kg/h)                     | 340       | 0         | 340       |
| $\text{TiCl}_4$ (t/h) for 1st stage                                     | 9.1       | 1.2       | 24.0      |
| 2nd stage                                                               | 14.9      | 2.9       | -         |

|           |   |     |   |
|-----------|---|-----|---|
| 3rd stage | - | 4.3 | - |
| 4th stage | - | 6.5 | - |
| 5th stage | - | 9.1 | - |

5 The method according to the invention offers several advantages compared to the addition of gaseous  $\text{TiCl}_4$ :

- The energy and apparatus required for evaporating the  $\text{TiCl}_4$  are eliminated.
- Because of the high momentum of the injected liquid droplets, the  $\text{TiCl}_4$  can be dispersed more efficiently when added in liquid form, this making it possible to create more homogeneous reaction conditions.
- In the multi-stage method, mixing with relatively cold educt in the second and further combustion stages lowers the adiabatic reaction temperature, meaning that the sintering process, i.e. particle growth, is completed sooner. This reduces the content of coarse particles in the pigment.

15 Figures 1 to 6 show exemplary embodiments of the invention. Figures 1 and 2 show a plug flow reactor (10). The introduction of liquid  $\text{TiCl}_4$  (14) is performed e.g. through nozzles (12) which are aligned around the circumference of the reactor (10). The liquid  $\text{TiCl}_4$  (14) is atomized into small droplets (16) by nozzle (12), the droplets evaporate within the reactor (10) without hitting the walls of reactor (10). Figure 2 illustrates the direction (18) of the gas flow within the reactor (10). Nozzle (12) is preferably enveloped effectively by a protective gas (20) additionally introduced into the reactor (10) in order to prevent any accumulation of solids and thermal damage to nozzle (12). Figure 1 illustrates nozzle (12) aligned parallel to a plane lying perpendicularly to the center line of reactor (10).

25 Figures 3 and 4 show a preferable embodiment of the invention, wherein a hollow cone cluster head nozzle (22) is used which atomizes the introduced  $\text{TiCl}_4$  (14) into smaller size droplets (24) in comparison to the single fluid nozzle (12). In another embodiment of the invention two fluid nozzles are used instead of the single fluid nozzles (12) and (22), where a liquid like  $\text{TiCl}_4$  and a gas (propellant), can be introduced simultaneously into the reactor (10). As a propellant one gas or a mixture of the gases from the group comprising nitrogen, argon, chlorine gas and oxygen may be used.

35 Figure 5 shows an embodiment of the invention wherein the nozzles (12) are aligned radially to the circumference of reactor (10) and parallel to a plane lying perpendicular to the center line of the reactor (10). Liquid  $\text{TiCl}_4$  (14) is introduced through the nozzles (12) into the reactor (10) and atomized.

Figure 6 shows a further embodiment of the invention wherein the nozzles (12) are aligned tangentially to the circumference of the reactor (10) and in a plane lying perpendicular to the center line of the reactor (10). Liquid  $\text{TiCl}_4$  (14) is introduced through the nozzles (12) into the reactor (10) and atomized. Due to the tangential orientation of the nozzles (12) the flow within the reactor (10) is set in rotary motion. By this, the distribution of the abrasive particles introduced into the reactor (10) to clean the interior walls of reactor (10) according to prior art is improved.

- 10 The practical examples described are merely possible embodiments of the invention and not to be taken as restricting the invention. For example, the present invention optionally also comprises the addition, familiar to the person skilled in the art, of additives for rutilisation (e.g.  $\text{AlCl}_3$ ) and for nucleation (e.g. alkali salts) in the reaction zone.
- 15 Furthermore, the present invention comprises embodiments of the method characterised by multistage addition of oxygen.

## CLAIMS

- 5           1. Method for manufacturing titanium dioxide particles by reacting titanium tetrachloride with an oxygen-containing gas in a plug flow reactor, characterised in that the titanium tetrachloride is introduced into the reactor in at least two stages and is used exclusively in liquid form.
- 10           2. Method of Claim 1, characterised in that the titanium tetrachloride is introduced by single-fluid nozzles, particularly by hollow-cone cluster-head nozzles.
- 15           3. Method of Claim 1, characterised in that the titanium tetrachloride is introduced by two-fluid nozzles.
- 20           4. Method of Claim 3, characterised in that a propellant selected from the group comprising nitrogen, argon, chlorine gas or mixtures thereof is used.
5. Method of any of Claims 2 to 4, characterised in that the nozzles are enveloped by a protective gas.
- 25           6. Method of any of Claims 2 to 5, characterised in that the nozzles are aligned parallel to a plane lying perpendicularly to the centre line of the reactor.
- 30           7. Method of Claim 6, characterised in that the nozzles are aligned tangentially to the circumference of the reactor.
- 35           8. Method of any of Claims 1 to 7, characterised in that the oxygen is preheated to a temperature of up to roughly 1,600 °C, preferably to a temperature in the range from roughly 740 °C to 1,000 °C.